

1.162.517



## PATENT SPECIFICATION

NO DRAWINGS

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## COMPLETE SPECIFICATION

## Process for the production of Polyurethane Foams

We, THE DUNLOP COMPANY LIMITED (formerly Dunlop Rubber Company Limited), a British Company of Dunlop House, Ryder Street, St. James's, London S.W.1 (formerly of 1, Albany Street, London, N.W.1.), do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for the production of polyurethane foams and in particular to a method of producing moulded flexible polyurethane foam articles without the need for high temperature curing.

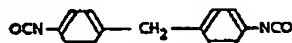
Polyurethane foams are obtained by the reaction of a polyol and a polyisocyanate (or polyisothiocyanate) in the presence of a blowing agent. The blowing agent is conveniently carbon dioxide obtained *in situ* as a result of the reactions by which the polyurethane is formed. For example, a foam-forming composition can be prepared by reacting a polymeric polyol and polyisocyanate to give a polyurethane prepolymer having free isocyanate groups, which is then reacted with a compound, for instance water, containing active hydrogen atoms to effect generation of carbon dioxide which foams the resulting polyurethane. Polyurethane foams can alternatively be obtained by what is known as a "one-shot" process in which a polymeric polyol, a polyisocyanate and an active hydrogen atom-containing compound, together with any other ingredients required, are mixed together and reaction of the ingredients of the composition produces a polyurethane which is concurrently foamed by carbon dioxide generated in the process.

Where the desired polyurethane foam is for use in the production of large articles such as mattresses, the reactants are conveniently mixed together and the mixture poured into a tray, the polyurethane thereby produced being foamed by the carbon dioxide generated in the

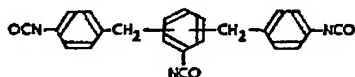
reaction to give a self-supporting "loaf" of polyurethane foam which after gelling can be cut into the desired articles. However, where the polyurethane foam products to be made are smaller articles of more intricate shape, for instance seat cushions, the "loaf" process is not nearly so convenient and it is often preferable to form the polyurethane foam in a closed mould by feeding the mixture of reactants into the mould, closing the mould and allowing sufficient time for the polyurethane foam to be formed and to gell to the shape of the mould. However, in this latter process using conventional polyisocyanates such as tolylene di-isocyanate, it is necessary to subject the moulded article to an additional maturing stage which normally comprises removing the moulded article from the mould and heating it in a hot-air oven. This additional stage is inconvenient and increases the cost of the moulded products because of the increased time of the production cycle, the space required to accommodate the ovens and their high capital cost and the fuel necessary to heat them.

According to the present invention we have devised a process by means of which moulded polyurethane foam articles can be obtained without the need of the additional stage referred to above. According to one aspect of the invention, therefore, flexible polyurethane foam articles are produced by the inter-action of a polymeric polyol with an organic polyisocyanate using carbon dioxide or other blowing agent, in which the polyol is a polyoxypropylene having chain terminal groups derived from ethylene oxide, the polyisocyanate is one having 2, 3 or 4 benzene rings, each carrying at least one isocyanate group, the rings being attached to one another by means of methylene groups, and the reaction mixture containing the polyol and polyisocyanate is fed into a mould and allowed to cure without the application of heat. The polyisocyanate is preferably one of the commercial products known

as M.D.I. or P.A.P.I. M.D.I. is a diisocyanate of the formula:



5 and P.A.P.I. is a stabilized mixture of di-, tri- and tetra-isocyanates which contain approximately three isocyanate groups per molecule. Regarding the mixture simply as having three isocyanate groups per molecule it can be considered as being a mixture of isomers of  
10 the following general formula:



The polymeric polyol used in the process of the invention is conveniently a polyether triol having a molecular weight of 3000 to  
15 7000, especially 3000 to 5000, for instance 4800 to 5000. Although triols have been found to give very satisfactory results, the polyol does not necessarily have three hydroxyl groups and can be, for instance a tetrol or hexol or a  
20 mixture of polyols having different numbers of hydroxyl groups per molecule. However, whatever the nature of the polyol component it preferably has a hydroxyl value 24—56, especially 33—56, for instance 33—34.

25 The polyol may suitably be any block copolymer of propylene oxide, that is, 1,2-propylene oxide and ethylene oxide in which the greater part of the length of the polymer chain consists of groups derived from propylene oxide and a  
30 lesser part of the length of the chain at the ends thereof consists of groups derived from ethylene oxide. Suitable polyols are those known in the trade as "ethylene oxide tipped" polyols. The polyol may, for instance, be a diol produced by a block polymerisation initiated by water or a dihydric glycol, or the  
35 polyol may be a triol or a tetrol produced by a block polymerisation initiated by a polyhydric alcohol such as glycerol or a polyamine, for example. It is particularly preferred to use a glycerol-centred oxyethylene tipped polyoxypropylene triol.

45 Preferably a catalyst is included in the polyurethane foam-forming composition to accelerate cross-linking or chain extension of the foam composition, and substances conventionally used as catalysts in the production of flexible polyurethane foams can be used. Suitable catalysts are, for example, amine catalysts, for  
50 example one or more of triethylene diamine, N-dimethylethanolamine and N-methylmorpholine. Other suitable catalysts are metal compounds which are used conventionally as catalysts, for instance esters, alkyl esters and salts  
55 of the metal of Groups 4, 5 and 6 of the Periodic System, the metals of Group 4 being preferred, especially those in the A sub-group,

60 such as dialkyl tin diesters of fatty acids, for example dibutyl tin dilaurate, dibutoxy tin dilaurate, and divalent tin soaps such as stannous octoate, stannous iso-octoate and stannous oleate. If desired the catalyst can comprise a mixture of one or more amine catalysts and one or more metal compound catalysts.

The total amount of catalyst can be, for instance, 0.3—2%, especially 0.5—1.5% of the weight of the polyol.

70 A surface active agent may be used in the process of the invention but it is not essential. It can be any of the surface active agents conventionally incorporated in mixtures for the production of flexible polyurethane foams, particularly silicone oils, for instance poly siloxane-oxyalkylene block copolymers.

75 Where the blowing agent is carbon dioxide derived from the use of water in the reaction mixture the water may be incorporated in the reaction mixture as a liquid component or it may be provided in the form of steam supplied during the reaction. If the water is added as a liquid component the weight of water present will normally be in the range 2—5%, especially 2.5—3.5%, based on the weight of the polyol.

80 The polyurethane foam-forming composition can contain incidental ingredients, for instance foam stabilizing agents, pigments, fillers and auxiliary blowing agents.

85 The invention is illustrated by the following Examples.

## EXAMPLES 1—10

95 These Examples describe the production of flexible moulded polyurethane foam articles without the use of a separate curing stage.

The table below gives the ingredients used in each Example and the amounts by weight in which they were used. The polyol was a polyoxypropylene having chain terminal groups derived from ethylene oxide. In Examples 1—  
100 5 and 7—10 the polyol was one having a molecular weight of 5000, whereas in Example 6 it was one having a molecular weight of 3000. "Dabco" (Trade Mark) and "Propamine A" are respectively commercial triethylene diamine and N-dimethylethanolamine products. The silicone oil L. 520 is a poly methyl siloxane oxyalkylene block copolymer.

105 The foams were produced by the following procedure. The ingredients were formed into four reaction components as follows:—

- A — the polyol;
- B — a mixture of the water, amine catalyst or catalysts and silicone oil;
- C — the polyisocyanate; and
- 115 D — stannous octoate (where used) dissolved in a small portion of the polyol.

120 These four components were then fed concurrently to a quadruple-feed mixing head where they all were mixed together and the resulting mixture fed into a mould which was

then closed. Foaming and cross-linking of the foam took place in the closed mould without any processing difficulties, and a cured polyurethane foam product was obtained within 5 10 minutes of closing the mould. This time is, of course, considerably less than that required where the moulded product is cured in a hot air oven.

If a quadruple-feed mixing head is not available, the reaction mixture can be obtained by first mixing components A and B, then mixing in C and then D.

TABLE

Example No.	1	2	3	4	5	6	7	8	9	10
Polyol	100	100	100	100	100	100	100	100	100	100
Water	2.5	2.5	2.5	2.5	3.5	2.5	2.5	3.5	3.5	2.5
Catalysts										
"Dabco"	0.5	—	—	—	—	—	—	—	—	—
"Propamine A"	—	1.0	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
N-methyl morpholine	—	—	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Stannous octoate	—	0.4	0.4	0.4	0.4	0.5	0.2	0.2	0.2	0.2
Silicone oil	0.1	0.1	0.1	—	0.2	0.2	0.2	0.2	0.2	0.2
M.D.I.	44.4	44.4	44.4	44.4	59.4	50.1	50.1	66.5	66.5	—
P.A.P.I.	—	—	—	—	—	—	—	—	—	48.1
Freon II (trichlorofluoromethane)	10	10	10	10	10	10	—	10	—	10

## WHAT WE CLAIM IS:—

1. A cold-curing process for the production of moulded flexible polyurethane foam articles by the interaction of a polymeric polyol with an organic polyisocyanate, using carbon dioxide or other blowing agent in which the polyol is a polyoxypropylene having chain terminal groups derived from ethylene oxide, the polyisocyanate is one having 2, 3 or 4 benzene rings, each carrying at least one isocyanate group, the rings being attached to one another by means of methylene groups, and the reaction mixture containing the polyol and polyisocyanate is fed into a mould and allowed to cure without the application of heat.

2. A process according to Claim 1, in which the polyisocyanate is a diphenylmethane diisocyanate.

3. A process according to Claim 1, in which the polyisocyanate is P.A.P.I. (as hereinbefore defined).

4. A process according to Claim 1, 2 or 3, in which the polyol is a triol having a molecular weight of 3000 to 7000.

5. A process according to Claim 4, in which the polyol has a molecular weight of 4800 to 5000.

6. A process according to any of the preceding claims, in which the polyol has a hydroxyl value of 24 to 56.

7. A process according to Claim 6, in which the polyol has a hydroxyl value of 33—56.

8. A process according to any of the preceding claims, in which the polyol is "glycerol-centred".

9. A process according to Claim 1, substantially as described herein.

10. A cold-curing process for the production of moulded flexible polyurethane foam articles, substantially as described in any of the Examples.

11. A moulded flexible polyurethane foam article obtained by the process of any of the preceding claims.

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